

ENGINEERING RESEARCH INSTITUTE  
UNIVERSITY OF MICHIGAN  
ANN ARBOR

QUARTERLY REPORT NO. 3

September 1, 1953 to November 30, 1953

MONTHLY REPORT NO. 9

By

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Project 2120

U. S. RUBBER COMPANY  
SUBCONTRACT UNDER PRIME CONTRACT NOBS-55413 (NAVY BUREAU OF SHIPS)

November, 1953

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INTRODUCTION

The objective of the research under this contract has been to find new materials for capacitor films which will have superior electrical and mechanical properties. The work divides itself into two phases.

1. The reaction of anthracene with various materials to form 9,10-disubstituted anthracenes capable of undergoing condensation polymerization. It is necessary in this connection to find a new synthetic method, since the previously used 9,10-dichloromethylanthracene has proved to be an allergen.
2. The preparation of condensation polymers for evaluation as capacitor films.

During the fall quarter, we have investigated conditions for the preparation of condensation polymers. We have used anthracene-9,10-dipropionic acid and have explored different conditions for the preparation of polyesters with various glycols and polyamides with diamines.

The major effort on new synthetic routes has involved the addition of sodium to anthracene. Conditions have now been worked out so that condensation of 9,10-dihydro-9,10-disodioanthracene with materials such as ethylene oxide, epichlorohydrin, and halogenated esters can be tried.

SUMMARY OF EXPERIMENTAL RESULTS

As a result of a meeting with Mr. Sieffert of the U. S. Navy Bureau of Ships, and Dr. P. O. Tawney held in Ann Arbor on November 18, it was decided that an effort should be made to prepare polyesters of anthracene-9,10-diacetic acid with various glycols and copolymers of the diacetic acid,

the dipropionic acid and ethylene glycol. A fair share of our effort has been devoted to the preparation of the necessary starting materials. During this time, it was again emphasized that 9,10-dichloromethylanthracene is a particularly objectionable allergen when one of the workers on the project was incapacitated for several days. Work is proceeding now satisfactorily since his recovery.

At the request of Mr. Sieffert, samples of the polyesters prepared to date are being made in the form of films and wafers for electrical and mechanical testing in accordance with the specifications furnished by the Bureau of Ships.

Reproducible conditions have been found for the addition of sodium to anthracene in tetrahydrofuran solvent. Essential to the success of the preparation are maintaining the temperature near 25°C, use of very finely divided sodium (sodium dispersions of 20  $\mu$  particle size in toluene were obtained through the courtesy of National Distillers and these have been found to be very active) and appropriate control of the reaction time. The best conditions discovered to date yield 86% of acidic material, based on anthracene charged, after carbonation.

#### EXPERIMENTAL DETAILS

Reaction of a Polyester Having Hydroxyl End Groups With Hexamethylene diisocyanate. A sample of the polyester from anthracene-dipropionic acid and hexamethylene glycol with the latter in 20% excess was melted in a test tube at 150°C under a nitrogen atmosphere. A 50-mole-percent excess of hexamethylenediisocyanate was added. After ten minutes, the material was allowed to cool. The dark solid was dissolved in 50 ml of chloroform, and after filtration the polymer was precipitated by the addition of methanol. The softening point of this material was 125-130°C, essentially that of the starting polyester. It is apparent that reaction did not take place under these conditions. It is planned to repeat the experiment using longer reaction times and to conduct the reaction in solution rather than in bulk.

Preparation of Polyamides. Anthracene-9,10-dipropionic acid was converted into its hexamethylenediamine salt by reaction in absolute alcohol with a molar equivalent of hexamethylenediamine. When this salt was heated under a nitrogen atmosphere at 250°C for two hours, followed by further heating at the same temperature under a pressure of 1.5 mm for twelve hours, there remained a dark granular material which did not melt until heated above 300°C. In a similar way, mixtures of the anthracene salt with the hexamethylenediamine salt of adipic acid (6-6 Nylon salt) were prepared and

polymerized. Varying the mole ratio of the two acids to as high as three parts of adipic acid to one part of anthracene acid did not form polymers of any lower softening point. All polymers obtained were highly insoluble in organic solvents, including dimethylformamide, so that it appears that these materials are likely to be unsuitable for a capacitor film in view of the anticipated difficulty in their fabrication. Attempts will be made to mold these polyamides in a Carver Press so that they may be tested electrically.

Preparation of Polyesters from Anthracenedipropionic Acid and Glycols. In addition to the previously reported synthesis of polyesters by ester interchange, it was found that polyesters could be prepared by the zinc chloride catalyzed esterification of the free acid with the glycol. The polymers obtained had essentially the same physical properties as previously described; namely, they would form good films by evaporation of chloroform solutions and they would form fibers when melted and drawn by a hot glass rod.

Addition of Sodium to Anthracene. Many exploratory experiments have been carried out, using recrystallized anthracene and sodium dispersion obtained from National Distillers Chemical Corporation in an atmosphere of deoxygenated nitrogen in tetrahydrofuran solvent freshly distilled from sodium. In an experiment typical of the best conditions found, from 0.0368 mole of anthracene and 0.0735 atom of sodium dispersion in 100 ml of tetrahydrofuran, there was obtained after two hours of stirring followed by carbonation in a slurry of dry ice and tetrahydrofuran, 0.88 g. of neutral material, m.p. 208-211°C, which was shown to be unreacted anthracene. Three crops of acidic material were obtained: 4.70 g., m.p. 250-254°C dec., N.E. 167; 3.21 g., m.p. 283-286.5°C dec., N.E. 149; 0.74 g., m.p. 271-281°C dec., N.E. 140. The first crop apparently contains a small amount of the mono-carboxylic acid, but the second and third crop appear to be nearly pure dihydroanthracene-9,10-dicarboxylic acid as a monohydrate. The overall yield based on anthracene charged was 69% diacid, 17% monoacid, and 13.5% recovery of anthracene. The acids described were not recrystallized before determining their physical properties.

Reactions of 9,10-Dichloromethylanthracene with Magnesium. When the dihalide was stirred with excess magnesium in boiling tetrahydrofuran, no reaction was observed for six to eighteen hours. Formation of a flocculent precipitate then occurred. After further prolonged stirring, the suspension was carbonated on dry ice and acidified with ammonium chloride. The recovered magnesium corresponded to a consumption of two atoms of magnesium per mole of dihalide. Only a trace of acidic material was isolated.

The bulk of the dihalide appeared as a rather insoluble polymeric (?) substance. It could be separated into two fractions. One, about 20% of the weight of dihalide charged, contained halogen and was insoluble in 14 common

polar and nonpolar solvents. The other, about 60%, gave a negative Beilstein test for halogen, and was insoluble in hydrocarbon solvents and partially soluble in oxygenated materials. It dissolved completely in hot dioxane, from which it could be precipitated by water, m.p. 313-330°C.

It is suggested that the latter material is a polymer derived from 9,10-dimethyleneanthracene. This compound may have been formed in a manner analogous to that suggested for o- and p-dichloromethylbenzenes (Mann and Stewart, Chem. and Ind., Oct. 24, 1953).

Further work should be done on this reaction, but in view of the long reaction times and erratic results obtained with magnesium, it might be better to use a more active metal like sodium. The possibility will be explored.

